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Flow Behavior of a Cationic Biopolymer: Chitosan

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Summary

The effect of ionic strength (0.1 M $\leq$ [Cl] $\leq$ 0.4M), pH (3.0 $\leq$ pH $\leq$ 5.0) and shear rate (up to 1000 sec^{-1}) on the rheological response of concentrated chitosan solutions have been studied. It has been observed that viscosity increases with increasing chitosan concentration and that a shear thinning behavior is present for polymer concentrations above 0.50 g/dl. Also, it has been shown that the zero shear viscosity is independent of the ionic strength of the media, but increases as pH is increased. This behavior has been related to the role of the surface charge density on the chitosan backbone upon the intermolecular entanglement which control the rheological behavior of concentrated chitosan solutions.

Introduction

Chitosan is the best known deacetylated chitin derivative. It consists of unbranched chains of β (1-4) 2-amino-2 deoxy-D glucan residues. One of the unique properties of chitosan is its polycationic nature when dissolved in the appropriate solvent. It differs from other common natural resource available polysaccharides in that they are either neutral or anionic. This difference in the ionic character makes chitosan a very appealing polymer for a variety of industrial applications (1,2).

The rheological behavior of dilute chitosan solutions has been studied (3-4). These studies have shown the polyelectrolytic nature of chitosan, as well as the role of solution conditions when only intramolecular interactions and solvent-polymer interactions are involved. However, the evaluation of the influence of solution conditions upon the rheological response of concentrated chitosan solutions remains open. It is the objective of this study to estimate the effect of pH and ionic strength of the medium upon the rheology of concentrated chitosan solutions.

Material and Methods

Chitosan, Madera chitosan (Bio-Shell, Inc., Albany, Oregon) obtained from Tanner (snow) crabs, Chionicetes bairdi, was selected for this study. The chitosan sample had less than 1% of protein and ash, 80% deacetylation, and a molecular weight of 1.3 x 10^5. Solutions were prepared by stirring at room temperature chitosan powder in a 0.04 M HCl solution. After solubilization, analytical grade NaCl was added to adjust to the proper ionic strength. Then, the chitosan solutions were partially neutralized using standard NaOH-NaCl solutions until the desirable pH.

Chitosan solutions viscosities were measured with a Rheometric Mechanical Spectrometer (Rheometrics, Inc., Union-N.J.) at 25.0°C. A cone and plate geometry with a plate diameter of 50 mm, a cone angle of 0.019 radians and a strain of 20% was selected.

Results and Discussion

The rheological response of concentrated chitosan solutions as affected by pH with values between 3.0 and 5.0, salt concentration between 0.10 M NaCl and 0.50 M NaCl, and chitosan concentration between 0.50 g/dl and 1.50 g/dl are analyzed. Figure 1 shows the relationship between the shear viscosity and the shear rate for a representative set of conditions. Similar response is found for all other conditions evaluated in this study. The following features can be shown: 1) the shear viscosity increases with increasing chitosan concentration, 2) for the lower chitosan concentration, the solutions show a Newtonian behavior for the entire range of shear rate, and 3) for chitosan concentrations above 0.50 g/dl, the flow curves show a

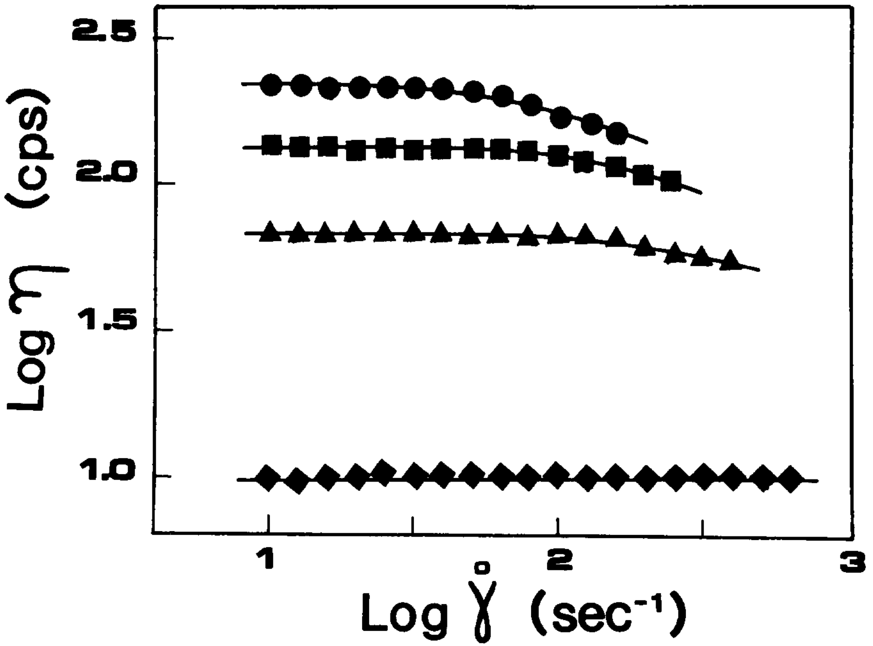

Figure 1: Shear rate dependence of steady flow viscosity of concentrated chitosan solutions: pH = 5.0; NaCl = 0.10 M. Symbols: ◆ :0.50 g/dl; ▲ :1.00 g/dl; ■ :1.25 g/dl; ● :1.50 g/dl chitosan concentration.

Newtonian region at low shear rate and shear thinning at high shear rates. This flow behavior of chitosan solution can be explained as the result of increasing intermolecular entanglement with increasing chitosan concentration and the reduction in the extent of entanglement coupling with increasing shear rate.

Figure 2 shows a plot of the zero shear viscosity as a function of pH and ionic strength of the medium. It can be observed that: 1) for the lower chitosan concentration, the zero shear viscosity is independent of both pH and salt concentration, and 2) with increasing chitosan concentration, the zero shear viscosity increases with increasing pH values but remains unaltered with changes in salt concentration.

The insensitivity of viscosity to ionic strength is atypical for polyelectrolytes. Generally, the viscosity of polyelectrolyte solutions decreases with increasing salt concentration due to smaller hydrodynamic radii (5). This typical behavior is observed in dilute chitosan solutions (6,7). However, the fact that the zero shear viscosity of concentrated chitosan solutions is independent of the salt concentration can be explained for the insensitivity of the surface charge density on the chitosan backbone

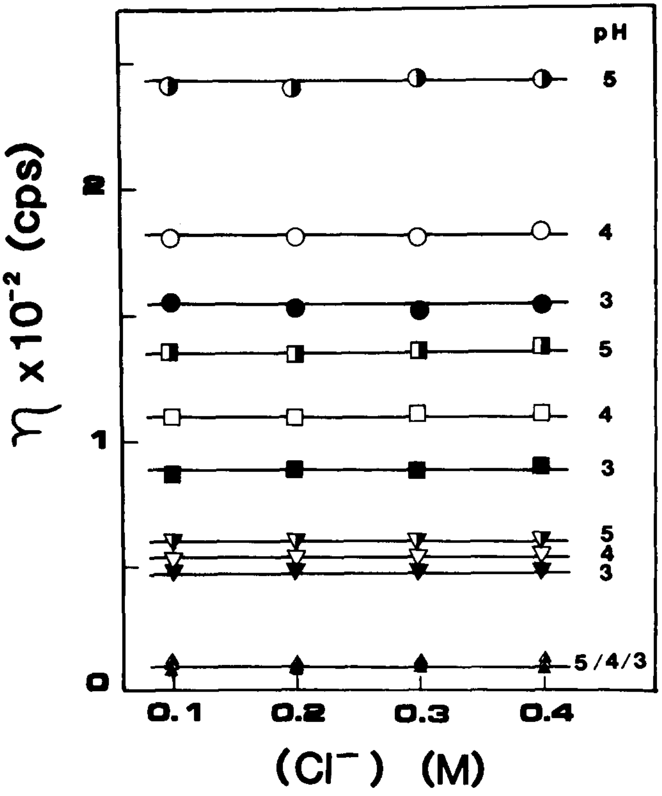

Figure 2: Zero shear viscosity of concentrated chitosan solutions as affected by pH and salt concentration. Symbols: ▲ :0.50 g/dl; ▼ :1.00 g/dl; ■ :1.25 g/dl; ● :1.50 g/dl chitosan concentration.

with changes in the ionic strength of the medium (7). The relationship between the surface charge density of chitosan molecules and entanglement coupling density was highlighted by the evaluation of the effect of medium conditions upon the relaxation mechanism of chitosan molecules in concentrated solutions (8). The zero shear viscosity insensitivity to salt concentration has also been reported for other polysaccharides in solution such as Xanthan gum (9-11) and alginate-KCl systems (12). Similarly, the influence of the pH, for chitosan concentrations above 0.50 g/dl, can be attributed to a decrease in the overall surface charge density on the chitosan backbone. The decrease of the surface charge density with increasing pH values was shown in potentiometric titration of concentrated chitosan solutions (7). This decrease in the overall charge density on the chitosan molecules induces an increase in the entanglement coupling by decreasing the intermolecular repulsive electrostatic forces. Meanwhile, the insensitivity of the zero shear viscosity for 0.50 g/dl chitosan solutions with changes in the pH can be attributed to low degree of intermolecular entanglements. This low degree of entanglement explains the Newtonian flow behavior of 0.50 g/dl chitosan solutions.

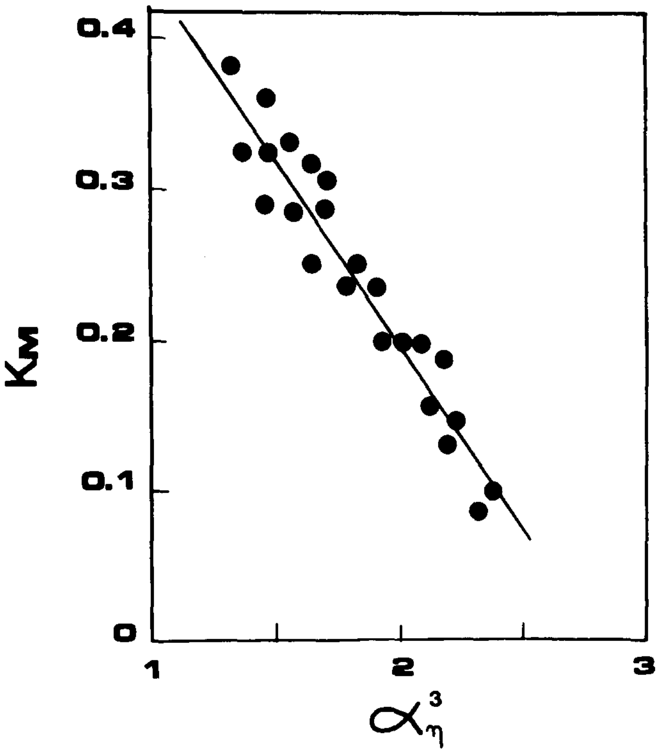

Figure 3: K_η from Martin's equations versus the electrostatic contribution to the expansion coefficient of chitosan molecules in solution.

These results show the controlling role of intermolecular interactions on the rheology of concentrated chitosan solutions. This controlling effect agrees with our previous findings in both counterion activity coefficients (13) and self-diffusion of small noninteracting particles (7) experiments.

The most common method of generalization for experimental results consists in the formulation of functional relationships of the form (14,15):

$$\frac{\eta_{sp}}{C[\eta]} = \bar{\eta} = \psi(C[\eta]) = \psi(\bar{C}) \qquad [1]$$

where $\bar{\eta}$ is the reduced viscosity function, $[\eta]$ is the intrinsic viscosity and $\bar{C}$ is the dimensionless concentration. The Martin's equation (15):

$$\bar{\eta} = \exp(K_M\bar{C}) \qquad [2]$$

is used to represent our data in both the diluted and the concentrated regimes.

Figure 3 shows the relationship between K_M and the electrostatic contribution to the expansion coefficient $(\alpha^3_{\eta e})$ of chitosan in solutions as obtained elsewhere (7). The decrease of K_M with increasing values of $\alpha^3_{\eta e}$ denotes the dependency of K_M on the polymer-solvent interactions as suggested by Dreval and coworkers for a variety of polymeric systems (16).

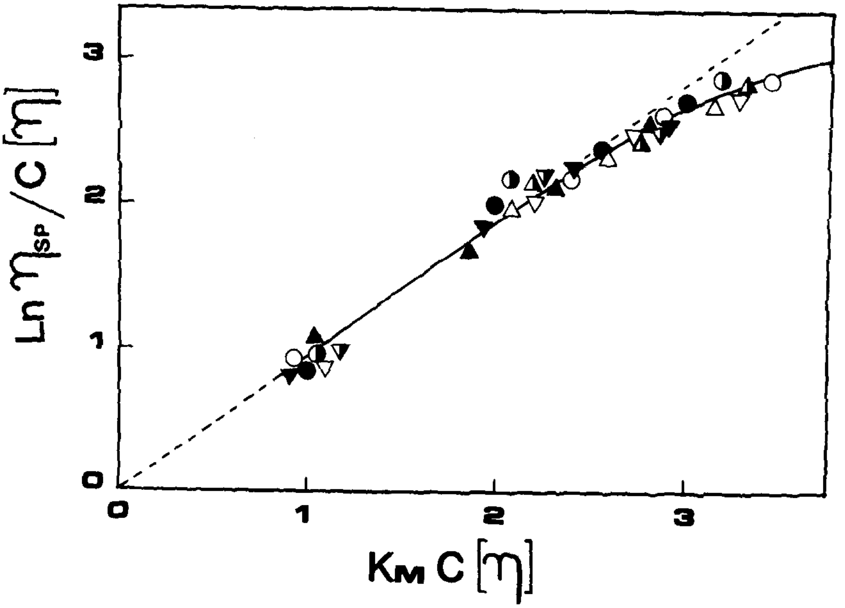

Figure 4: Logarithm of the reduced viscosity function versus K_M $C[\eta]$ for selected set of conditions. Symbols:

▲: pH = 5.0; NaCl = 0.50M
▼: pH = 5.0; NaCl = 0.30M
●: pH = 5.0; NaCl = 0.20M
△: pH = 3.0; NaCl = 0.50M
◐: pH = 6.0; NaCl = 0.10M
○: pH = 3.0; NaCl = 0.10M
▽: pH = 3.0; NaCl = 0.30M
◭: pH = 6.0; NaCl = 0.10M

Figure 4 shows the relationship between the logarithm of the reduced viscosity function and $K_M\bar{C}$ of a select set of conditions for concentrated chitosan solutions. A single line is obtained independently of the pH, salt and chitosan concentration. However, it can be observed a shift from the linearity for $K_M\bar{C}$ values higher than 2.0. This deviation from the Martin's equation is attributed to intermolecular associations as chitosan concentration increases. Similar behavior has been found in polymer solutions with high degree of entanglements (16,17).

In conclusion, the evaluation on the rheological response of concentrated chitosan solution suggests the importance of the relationship between surface charge density on the macromolecular backbone, intermolecular entanglement and flow behavior.

Acknowledgement

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